PB83-191205

Tungstic Acid Technique for Monitoring Nitric Acid and Ammonia in Ambient Air

(U.S.) Environmental Sciences Research Lab.
Research Triangle Park, NC

1982

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before comple

1. REPORT NO. EPA-600/J-81-462	2. JOURNAL ARTICLE
3 PB83-191205	
4. TITLE AND SUBTITLE TUNGSTIC ACID TECHNIQUE FOR MONITORING NITRIC ACID AND AMMONIA IN AMBIENT AIR	5. REPORT DATE 1982
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) W. A. McClenny, P. C. Gailey, R. S. Braman and T. J. Shelley	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Sciences Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, N. C. 27711	10. PROGRAM ELEMENT NO. CDWA1A/ 9-1170 FY-81
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, N. C. 27711	13. TYPE OF REPORT AND PERIOD COVERED
	14. SPONSORING AGENCY CODE EPA/600/09

15. SUPPLEMENTARY NOTES

Anal. Chem. 54:365-369 (1982)

16. ABSTRACT

A new measurement procedure has been applied in field studies for monitoring ambient concentrations of HNO_3 and NH_3. Preconcentration of these gases as well as separation from their particulate forms is achieved by pulling the sampled air through a diffusion tube coated with the amphoteric sorbent, tungstic acid. Thermal desorption releases NH_3 as NH_3 and HNO_3 as NO_2 for analysis in a standard chemiluminescence NO_x monitor. Results of field tests in Hampton, Va., Research Triangle Park, N. C., and Croton, Ohio, demonstrate a unique combination of temporal resolution (40 min cycle) and of sensitivity (0.07 ppb) that allows the monitoring of diurnal patterns at practically all monitoring sites. Features on the diurnal plots of HNO_3 show correlation with ambient O_3 during peak photochemical activity while average concentrations at the three sites appear to be related to local sources of NO_x. Diurnal plots of NH_3 appear to be the first such reported values at the sub-ppb level. The measurement procedure has been automated for sampling and analysis.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 6
	20 SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

EPA-600/J-81-462
JOURNAL ARTICLE

Tungstic Acid Technique for Monitoring Nitric Acid and Ammonia in Ambient Air

W. A. McClenny* and P. C. Galley

U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711

R. S. Braman and T. J. Shelley

Department of Chemistry, University of South Florida, Tampa, Florida 33620

A new measurement technique has been applied to monitoring ambient concentrations of HNO_3 and NH_3. Preconcentration of these gases as well as separation from their particulate forms is achieved by pulling the sampled air through a diffusion tube coated with the amphoteric sorbant, tungstic acid. Thermal desorption releases NH_3 as NH_3 and HNO_3 as NO_2 for analysis in a standard chemiluminescence NO_x monitor. Results of field tests in Research Tringle Park, NC, and Croton, OH, demonstrate a unique combination of temporal resolution (40 min cycle) and of sensitivity (0.07 ppb) that allows the monitoring of diurnal patterns at practically all monitoring sites. At the NC site, HNO_3 and O_3 concentrations are positively correlated ($r = 0.80$) as HNO_3 concentrations vary from 1.3 to 0.4 ppb with highest values near midday. Semi real-time diurnal variations of NH_3 appear to be the first such measurements at the sub-part-per-billion level. The measurement procedure has been automated for sampling and analysis.

This paper supplements the preceding (*1*) by discussing the first applications of the tungstic acid integrative sampling technique. These applications involve measurement of ambient air concentrations of gaseous ammonia and nitric acid at two locations in the eastern U.S.A. The tungstic acid technique (TAT) has three major advantages when compared to other integrative sampling techniques for NH_3 and HNO_3: (1) minimal artifact formation; (2) semi real-time monitoring capability at sub-part-per-billion levels; (3) simultaneous collection of both gases. The same system can be slightly modified with the addition of a packed tube downstream of the diffusion tube so that NH_4^+ and NO_3^- in ambient particles can also be estimated. Other techniques for measurement of ambient NH_3 and HNO_3 are referenced in our companion article (*1*).

The major instances of artifact NH_3 and HNO_3 formation occur in the attempt to separate gaseous NH_3 and HNO_3 from their particulate forms. The use of diffusion tubes to effect this separation appears to be superior in this regard to the use of tandem filters (the other commonly used method). With tandem filters, the sample must pass through a particle collection filter before reaching a filter on which gases are collected. The accumulation of particles leads to a situation in which a number of possible interactions can occur to produce artifacts.

Ferm (*2*) has apparently shown one effect of in-line particle filters in his experiments to measure ambient ammonia. Separation of NH_3 by diffusion tube gave approximately 0.3 ppb as an average of 12 24-h sampling periods. The use of a Teflon Fluoropore (FALP) prefilter in an otherwise identical sampler increased the apparent NH_3 concentration to roughly 1.0 ppb during side-by-side, simultaneous sampling. Harward et al. (*3*) have documented significant losses of known trace concentrations of NH_3 when sampling through a filter loaded immediately before by sampling ambient air parcels containing nearby source emissions. Harker, et al. (*4*) observed artifact HNO_3 formation that they attributed to the release of HNO_3 from particulate nitrate as a result of reaction with acid sulfate. Shaw et al. (*5*) observed the release of ambient particulate nitrate collected on Teflon filters by comparing the amount of nitrate collected on a second in-line filter (nylon) with the ambient HNO_3 as determined by the denuder difference experiments (*6*). Up to 90% of the nitrate was lost from the Teflon filter. Other recent studies by Forrest et al. (*7*), Appel et al. (*8*), and Pierson et al. (*9*) have substantiated the various aspects of particle to gas and gas to particle conversion. The results of these and other experiments on artifact formation can be summarized as showing that a net exchange of NH_3 and HNO_3 can occur between the gas and aerosol forms at the filter surface.

With respect to artifact formation, conclusions to be drawn from previous research are as follows: (1) the use of tandem filters should be considered a less desirable alternative than the use of diffusion tubes; (2) since the accumulation of particles on prefilters makes interactions increasingly probable, sampling time should be minimized; (3) release of gases from particles during transit of diffusion tube collector/separators should be minimized by limiting the residence time.

In the use of diffusion tubes, collection of gases at the diffusion tube wall during sample transit is assumed to occur more rapidly than the release of gases from ambient particles in the process of reestablishing equilibrium in the altered sample. The gases adsorbed on the diffusion tube then closely represent the amount of NH_3 and HNO_3 in the gas phase during a collection period. The question of the relative magnitude of the diffusion and release processes has not yet been adequately investigated. However, Durham and Spiller (*10*) have shown that release of HNO_3 does occur to a considerable extent (70% in their experiments) from particles containing volatile nitrates if the residence time of sample air in the diffusion tube is sufficiently long (2.2 s). Ferm (*2*), as well as Appel et al. (*11*) do not observe this release for short residence times, 0.3 s for NH_3 and 0.25 s for HNO_3, in their respective experiments.

The sensitivity of the TAT system is such that 0.07 ppb, of either NH_3 or HNO_3, collected for 20 min at a sampling rate of 1.0 L/min results in a minimally detectable response. For HNO_3 this sets the minimum detectable ambient concentration and loading (4 ng) since the WO_3-coated tubes develop minimal blank values. For example, in a recent field trial, tubes were carried through field excursions without being used and then analyzed; in 14 of 16 cases the HNO_3 blank values were undetectable. For NH_3, variability in blank values sets the minimum detectable ambient concentration if significant time elapses between sampling and analysis. In a set of 16 control tubes the average blank value approximately 4

Published in Analytical Chemistry, March, 1982, pp. 365–369, by the American Chemical Society

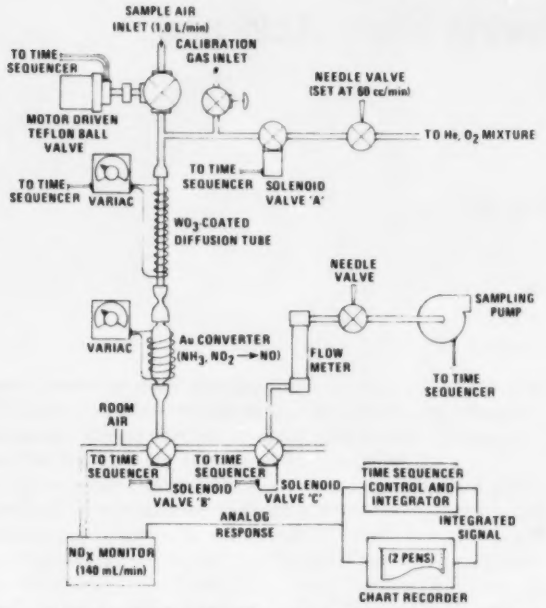

Figure 1. Automated tungsten(VI) oxide technique for ambient HNO_3 and NH_3 detection.

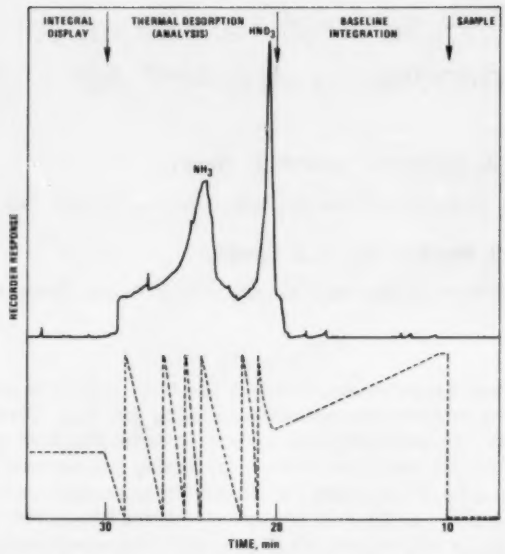

Figure 2. Typical trace from EPA automatic sampler showing results of thermal desorption from WO_3-coated diffusion tube. Dotted line indicates integrator output.

h after collection was 19 ng with a standard deviation of 4.5 ng. The 4.5 ng variability corresponds to an ambient concentration of 0.3 ppb. Automatic samplers reduce this variability since no appreciable time elapses between collection and analysis.

EXPERIMENTAL SECTION

Data were gathered, using the TAT in two configurations, manually, as described by Braman et al. (*1*), and automatically using a prototype system designed at EPA, Research Triangle Park, NC. Peak separations for NH_3 and HNO_3 (as NO_2) in the manual technique were shown in Figure 5 of the preceding paper (*1*). The automated sampler utilizes the timing electronics and integrator from an existing unit (*12*) to perform cyclic operation of the technique. Typically, it takes one 20-min sample every 40 min using the remaining 20 min for analysis, cooling of the diffusion tube, and display of the HNO_3 and NH_3 integral. The following detailed description of the four-step cycle can be understood by refering to Figure 1: (1) trapping (10–50 min), ball valve open, sampling pump on, ambient air is drawn through the inlet at 1.0 L/min, trapping the NH_3 and HNO_3 on the diffusion tube walls; transit time for the sample is 0.3 s; (2) base line (10 min), trapping continues as above while the base line signal is integrated; the base line integration time of 10 min is equal to the analysis integration time; (3) analysis (10 min) ball valve closes, solenoids A and B are activated, the diffusion tube heating coil is activated, sampling pump stops, He–O_2 mixture (80%, 20%) entrains the desorbed NH_3 and NO_2 which is converted into NO as it passes through the Au convertor and is routed to the NO_x monitor for measurement, integration of the peaks takes place; (4) integral display (10 min), ball valve open, solenoids A and B deactivated, diffusion tube heating coil off, sampling pump on, solenoid C activated to supply sampling pump, diffusion tube cools as the net integral (integral of signal during analysis minus integral of signal during base line) is displayed.

A typical recorder trace showing both an analog signal from the NO_x monitor and the integrator response is shown in Figure 2. The first peak is the signal resulting from HNO_3 desorbed as NO_2 and the second peak is due to NH_3 desorbed as NH_3. The integrator response initially decreases from an offset "zero" during a count-down sequence as the base line is being integrated and then counts up by an amount proportional to the integral of the analog signal developed during the analysis phase. The net length of the integrator response display (dotted line) is proportional to the amount of NH_3 and NO_2 released from the diffusion tube wall. By use of the change in slope of the integrator response as an indicator, the contributions due to NH_3 and to HNO_3 can be separated. The constant offset of the base line, evident in Figure 2 during thermal desorption, is present even with sampling air containing no HNO_3 or NH_3. The exact cause of the offset has not been isolated. Its contribution to the signal integrals is subtracted.

Both packed and hollow tubes can be used in this apparatus. Packed tubes give total NH_3 and HNO_3 and approximately 80% of particulate NH_4^+ and NO_3^-. Packed tubes used in early preliminary work were replaced with a hollow tube so that only values for gaseous NH_3 and HNO_3 were obtained. Separation of the peaks shown in Figure 2 was achieved by careful selection of the voltage setting of the diffusion tube heater variac rather than through the use of a transfer tube as described by Braman et al. (*1*). As a consequence the response peaks, especially for NH_3, are not as distinct nor as well separated. One other difference is the use of 20% O_2 in the He carrier gas stream that is used during thermal desorptions. Oxygen was added to the carrier gas to ensure its presence in the conversion process (NO_2, NH_3 → NO). An undesirable consequence is that a small but variable percentage of collected ammonia is converted to nitric acid during analysis.

Nitrogen compounds are converted to NO during analysis by passing them through a high-temperature converter. Early versions of the converter employed gold-plated sand in a quartz tube as the catalyst. This design had the disadvantage of introducing a relatively large resistance into the flow path thus increasing the likelihood of leaks in the system. An alternate design, consisting of coils of gold foil in a quartz tube eliminated this problem and was used in later studies. Nitric oxide was measured by using a Bendix Model 8001 NO_x monitor operated in the "NO only" mode. The sensitivity of the monitor was enhanced by reducing the pressure in its reaction chamber to 10–40 torr. Pressure was reduced by attaching a small capacity Welch Duo Seal oil pump to the reaction chamber exhaust lines.

Ammonia standards for calibration were either commercially available permeation tubes (Metronics, Inc.) or permeation tubes made in the lab. The weight loss rate for these tubes at constant temperature was measured on a Cahn electrobalance. Subsequently, the tubes were placed in a constant temperature enclosure that was flushed continuously with ammonia-free, zero air. The high gaseous concentrations thus established were either sampled directly for short periods (1–10 s) to simulate typical ambient loadings or further diluted before sampling. Ammonium sulfate and ammonium bisulfate solution standards were prepared and placed on packed tubes containing tungsten oxide coated beads.

Table I. Comparison of NH_3 and HNO_3 Concentrations at Different Locations

site, date	amt of NH_3, ppb			amt of HNO_3, ppb			no. of readings
	av	high	low	av	high	low	
Res. Tri. Park, NC, July 80	0.45	0.96	0.25	0.86	1.30	0.32	43
Columbus, OH, Aug 80	2.16	7.76	0.63	0.70	3.85	0.12	157

Both sets of readings were consistent with the gas standards; i.e., linear regression analysis gave slopes that agree within 6%. MTAT calibration curves taken 4 months apart in different field studies agree to within 5%. ATAT calibration runs showed greater variability with time and frequent daily calibrations were necessary to assure accuracy of results. This variability is at least in part due to a variable reaction chamber pressure in the NO_x analyzer and, in the early studies, to the variable restriction of the NO_2, NH_3 converter.

Nitric acid calibrations were performed by using a capillary diffusion tube in the same manner as a permeation tube. The ATAT again exhibits greater variability in response to calibration mixtures. In one field test the NH_3 calibration curve was also used for HNO_3 calibration, i.e., both were treated as sources of a NO molecule. A single check of equality of response to equal concentrations of HNO_3 and NH_3 showed that NH_3 gave a slightly higher response per molecule, 1.12 of that for HNO_3. ATAT measurements for ten 54.6-ng loadings gave a standard deviation of 5%.

RESULTS AND DISCUSSION

Initial TAT applications include two short-term field studies of ambient HNO_3 and NH_3 concentrations. The field studies occurred at Research Triangle Park (RTP), NC, 30 June–3 July, 1980, and Croton, OH, 10–15 Aug, 1980. The ranges of concentrations and the average concentrations are listed for two sites in Table I. The variation in ratio of HNO_3 to NH_3, i.e., from 2.0 at RTP to 0.3 at Croton is probably a result of the influence of local sources. The RTP site is in a rural setting but near a parking lot and local roadway from which NO_x emissions probably enhance the production of HNO_3. The Croton site is in a rural area near a livestock holding area. This location probably accounts for the high average and high upper limit values of NH_3. HNO_3 values are in the range of typical background values, <0.1–3 ppb (*13*) as expected from the location of the two relatively isolated monitoring sites.

Measurement precision for the MTAT was estimated from the comparison of results obtained during side-by-side, simultaneous ambient air measurements at RTP, NC. A set of 21 paired measurements was examined to compute the average value of the ratio Δ/Σ where Δ denotes a difference between duplicate measurements and Σ denotes a sum of the duplicate measurements. Expressed as a percentage, $(\Delta/\Sigma)_{av}$ = 4.4% for HNO_3 and 6.9% for NH_3. These values were not dependent on the amount of gas collected and appear to result from some other system parameter, possibly the setability of flow rates for the two separate collection devices or the response peak integration accuracy. The $(\Delta/\Sigma)_{av}$ values were taken as a measure of precision.

The MTAT values for precision and sensitivity compare favorably with other techniques for ambient NH_3 and HNO_3. For example, values given by Ferm (*2*) show that in a set of 12 24-h sampling periods his NH_3 monitoring technique gave a $(\Delta/\Sigma)_{av}$ value of 4.0% and an analytical limit corresponding to 0.001 ppb. Shaw et al. (*5*) measured ambient nitric acid and reported values that correspond to a $(\Delta/\Sigma)_{av}$ = 11.0% for nine 23-h samples and an analytical limit of detection corresponding to 0.05 ppb using the denuder difference experiment (*6*).

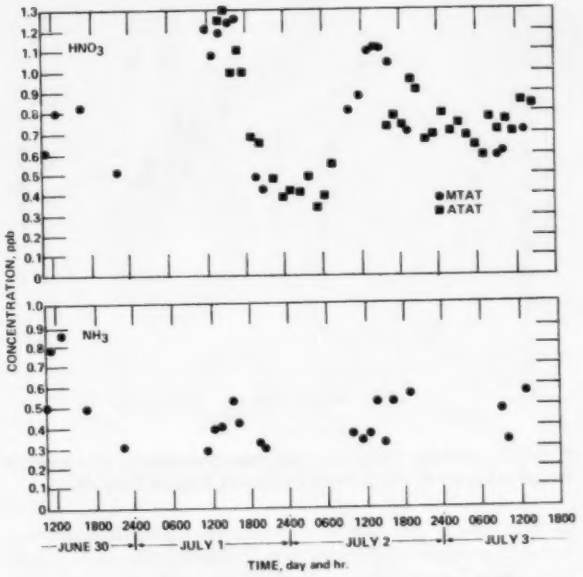

Figure 3. NH_3 and HNO_3 concentrations over 4-day period at Research Triangle Park, NC.

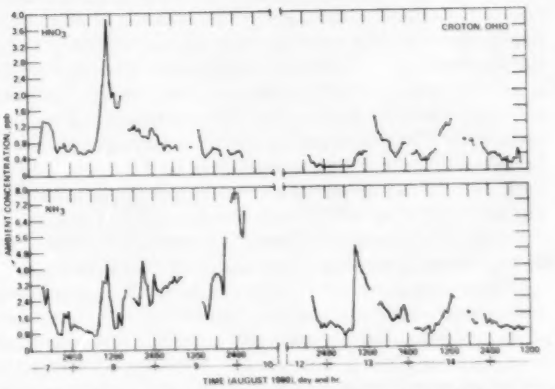

Figure 4. NH_3 and HNO_3 concentrations measured over 8-day period at Croton, OH, using EPA automatic sampler.

The ATAT is less sensitive than the MTAT due to the broadening of response peaks; e.g., compare Figure 2 of this paper and Figure 5 of the previous paper. Improvement in sensitivity is anticipated if a transfer tube is incorporated into the ATAT system to separate NO_2 (resulting from thermal desorption of HNO_3) and NH_3. The ATAT would then be identical in operation with the MTAT.

Diurnal variations with either half-hourly or hourly readings were recorded. The RTP readings for HNO_3 were taken with both the MTAT and the ATAT. These values along with NH_3 values taken with the MTAT are shown in Figure 3 for the period 30 June–3 July, 1980. Average HNO_3 values during the periods of common reading were 0.83 ppb for the MTAT and 0.90 ppb for the ATAT. Since the ATAT readings were usually taken with hourly sampling periods as compared to the 20-min MTAT sampling periods, the disagreement of 0.07 ppb between the techniques is not unreasonable. Similar data (Figure 4) were taken at Croton, OH, with the ATAT, giving an additional example of NH_3 and HNO_3 variations.

Both sets of data exhibit similar diurnal patterns in HNO_3 concentrations. Maximum HNO_3 values occur near midday and relative minimum values in the early morning, with a variation in the ratio of relative maximum to relative minimum

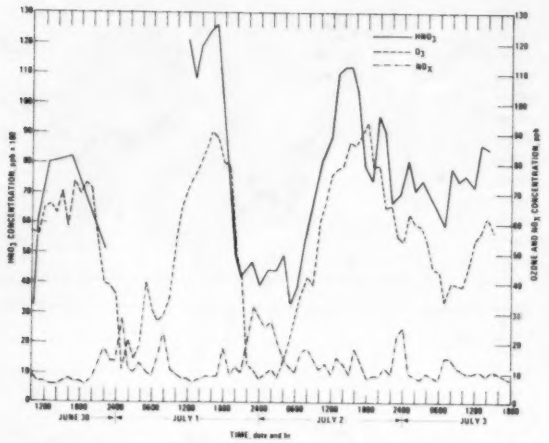

Figure 5. Ozone, HNO_3, and NO_x variations during field trials of tungsten(VI) oxide technique at Research Triangle Park, NC.

of from 4 to 2. In some cases, relatively high HNO_3 concentrations persisted during the night. Similar diurnal patterns have been documented by Battelle Columbus Laboratories (*14*) in West Covina, CA, and in more recent studies near Van Hiserville, NJ (*13*). Midday maxima are explained (*13*) as due primarily to the accumulation of HNO_3 as the product of the reaction between NO_2 and OH, while the loss of HNO_3 at night and the variability of absolute HNO_3 concentrations were due to a combination of HNO_3 sinks and of transport of different air masses into the study area. The correlation of ambient ozone with HNO_3 as expected from the previous studies can be seen in Figure 5 for the field trial at Research Triangle Park, NC. HNO_3 values are a composite of values taken from Figure 3, deleting ATAT values when MTAT values are available. The correlation coefficient was 0.80 for HNO_3 and O_3 variations, assuming no measurement error in ozone.

Diurnal variations of NH_3 with the sensitivity and temporal resolution shown in Figures 3 and 4 have apparently not been previously published, although this capability has been shown by at least one other technique (*15*). Ammonia concentrations are noted to exhibit a pronounced diurnal pattern peaking in the morning or near midday, slightly before maximum HNO_3 values are reached. Ratios of relative maximum to minimum concentrations vary from about 4 to 2, similar to the HNO_3 ratios. Ammonia variation is presumed to be due to its increased generation at the surface as a function of ambient ground level temperatures leading to evaporation of H_2O and release of dissolved NH_3 (*16*). Midday and afternoon decreases in NH_3 may be due to the reaction between NH_3 and OH radicals, to the reaction of NH_3 with photochemically generated acid aerosols and/or depletion of NH_3 available from groundwater evaporation. In most cases higher HNO_3 maxima seem to be correlated with lower NH_3 maxima. Evidence of nighttime relative maxima for NH_3 and HNO_3 at Croton and a trend of increasing average NH_3 concentration during 8–10 August at Croton may be due to a combination of meteorological conditions, i.e., wind direction and/or low level inversions, that favor concentration buildup. Several of these possibilities can be developed by using data taken at the same site near Croton and now being processed by Wilson and McMurray (*17*).

Reduction in the collection efficiency (poisoning) of diffusion tubes can occur during ambient sampling. This behavior has been observed in two notable cases during recent ambient monitoring. In one case, the diffusing plume from a nearby coal-fired power plant was sampled; in the other case, at a remote site, the sampled air mass contained particulate matter that significantly reduced visibility. The cause of this poisoning has not been identified. As explained elsewhere (*1*), the collection efficiency can be restored by reconditioning the tubes. During ambient sampling runs, frequent calibration checks should be used to identify any reduction in collection efficiency.

The TAT has been compared with two other techniques. Shaw et al. (*5*) reports that integrated values over two 23-h sampling periods using the denuder difference technique (*6*) gave values of 1.9 and 2.2 ng/L for HNO_3 while the TAT averaged values for the same time periods were 2.2 and 1.9 ng/L. Harward et al. (*3*) gives ambient NH_3 comparison of 0.85 ng/L (Teflon bead technique (*19*)) and 1.05 ng/L (TAT) as average values for nine side-by-side sampling runs of 20 min each. In both cases the individual techniques were independently calibrated.

A further application for the TAT is in the sampling of air masses from aircraft. The diffusion tubes and sampling gear present an alternative to larger real-time instrumentation since a sample can be obtained in a time sufficiently short (1–10 min depending on concentration) to make aircraft sampling feasible. Limited studies of this type have been done in the Columbus, OH area (*20*); NH_4^+ and NO_3^- in particles were also estimated by using a packed tube downstream of the diffusion tube for collection. The monitoring of HNO_3 and NO_3^- in dispersing power plant or urban plumes as well as NO and NO_2 should provide a basis to calculate conversion rates, i.e., $NO_2 \rightarrow HNO_3$, $HNO_3 \rightarrow NO_3^-$. Combined with other existing instruments such as the NO_x chemiluminescence analyzer and gas chromatography–electron capture for analysis of PAN, the ATAT can be used to great advantage to more accurately measure the transport and transformation of N-containing compounds.

ACKNOWLEDGMENT

The authors acknowledge the assistance of the following people in performing the field tests: J. M. Hoell, C. N. Harward, J. S. Williams, and B. S. Williams of NASA Langley Research Center, J. C. Wilson and P. H. McMurray of the Mechanical Engineering Department, University of Minnesota, and R. W. Shaw, Jr., and R. K. Stevens of EPA, Research Triangle Park, NC. Thanks also to G. Gallant and R. Barbour for preparation of the manuscript.

LITERATURE CITED

(1) Braman, R. W.; Shelley, T. J.; McClenny, W. A. *Anal. Chem.*, preceding paper in this issue.
(2) Ferm, M. *Atmos. Environ.* **1979**, *12*, 1385–1393.
(3) Harward, C. N.; McClenny, W. A.; Hoell, J. M.; Williams, J. A.; Williams, B. S., NASA Langley Research Center, Hampton, VA, unpublished work, 1980.
(4) Harker, A. B.; Richards, L. W.; Clarke, W. E. *Atmos. Environ.* **1977**, *11*, 87–91.
(5) Shaw, R. W., Jr., Stevens, R. K.; Bowermaster, J.; Tesch, J. W.; Tew, E. *Atmos. Environ.*, in press.
(6) Shaw, R. W., Jr., Dzubay, T. G.; Stevens, R. K. "The Denuder Difference Experiment", U.S. EPA Research Report EPA-600/2-79-051; U. S. Environmental Protection Agency: Research Triangle Park, NC, 1979.
(7) Forrest, J.; Tanner, R. L.; Spandau, D.; D'Ottavio, T.; Newman, L. *Atmos. Environ.* **1980**, *14*, 137–144.
(8) Appel, B. R.; Wall, S. M.; Tokiwa, Y.; Haik, M. *Atmos. Environ.* **1980**, *14*, 549–554.
(9) Pierson, W. R.; Brachaczek, W. W.; Korniski, T. J.; Truex, T. J.; Butler, J. W. *J. Air Pollut. Control Assoc.* **1980**, *30*, 30–34.
(10) Durham, J. L.; Spiller, L. L., U.S. Environmental Protection Agency, Research Triangle Park, NC, private communication, 1980.
(11) Appel, B. R.; Tokiwa, Y.; Haik, M. *Atmos. Environ.* **1981**, *15*, 283–289.
(12) Hrubesh, L.; Barton, V. "Ammonia Preconcentrator/Integrator-Instrument Manual" Report UCID-17174; Livermore National Laboratory: Livermore, CA, 1975.
(13) Spicer, C. W.; Sverdrup, G. M. "Trace Nitrogen Chemistry during the Philadelphia Oxidant Data Enhancement Study (1979)". Final report Contract No. 68-02-3338; U.S. Environmental Protection Agency: Research Triangle Park, NC, 1979.
(14) Spicer, C. W. 1977 "The Fate of Nitrogen Oxides in the Atmosphere"; Pitts, J. N., Metcalf, R. L., Eds.; Wiley: New York, 1977; Vol. 7 Adv. Environ. Sci. Technol.
(15) Abbas, R.; Tanner, R. L. *Atmos. Environ.* **1981**, *15*, 277–281.

(16) Dawson, J. S. *J. Geophys. Res.* **1977**, *82*, 3125–3133.
(17) Wilson, J. C.; McMurray, P. H., Mechanical Engineering Department, University of Minnesota, Minneapolis, MN, private communication, 1980.
(18) Hoell, J. M., NASA Langley Research Center, Hampton, VA, private communication.
(19) McClenny, W. A.; Bennett, C. A., Jr. *Atmos. Environ.* **1980**, *14*, 641–645.
(20) Braman R. S.; Shelley, T. J. "Gaseous and Particulate Ammonia and Nitric Acid Concentrations—Columbus, Ohio, Area, Summer 1980"; EPA 600/7-80-179; U. S. Environmental Protection Agency: Research Triangle Park, NC, 1980.

RECEIVED for review May 20, 1981. Accepted October 9, 1981.